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3,725,068

PROCESS FOR THE PHOTOGRAPHIC DEVELOPMENT OF SILVER SALTS

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U.S. Cl. 96—66 HD

7 Claims

ABSTRACT OF THE DISCLOSURE

The present process for the photographic development of silver salts is carried out with 1,4-diazine compounds reduced at most to the dihydro stage. The latter are produced from the 1,4-diazines by reduction in situ in an acid medium.

This invention relates to the photographic development of silver salts.

It is characteristic of the known photographic processes for liberating silver from silver salts that the total amount of developer substance which forms the minimum requirement for the development process is present from the start of the reduction of the silver salts. In the known processes which contain the developer substance in the dissolved form liquids or pastes are preferably used. The developer substances can also be incorporated in the material containing the silver salt, or in a separate material which is brought into contact with the material containing the silver salt.

Developer substances are by nature reducing agents. They are oxidised by sufficiently strongly oxidising agents to products which are not capable of liberating silver from silver salts.

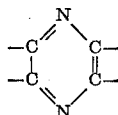
Their reactivity towards a great number of oxidising agents, e.g. towards atmospheric oxygen, has a detrimental effect on the stability of development substances, especially when these are present in dissolved state.

It is an object of the present invention to produce photographic processes and photographic materials which avoid this disadvantage.

From French patent specification No. 1,565,800 a process is known for the development of photographic silver images from silver salts which is characterised in that the silver is liberated from silver salts in acid medium with the help of reduction products of 1,4-diazines which have been reduced at most to the dihydro stage.

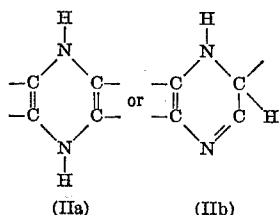
1,4-diazine compounds are compounds which contain at least ring of the formula

(I)



and which may, optionally, be substituted on the ring carbon atoms, in particular also by other ring systems condensed with them.

These compounds in order to be used as developer substances must be present in a reduced state in relation to the diazine. This state may be at an equilibrium somewhere between the diazine and the dihydro stage



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Furthermore the reduction products of diazines may be present in protonised form.

The redox and protonisation equilibria in which the 1,4-diazines and their reduction products, reduced at most to the dihydro stage, take part, are also presented in the U.S. Pat. No. 3,574,621.

Whereas the reduction products of the 1,4-diazines react readily with oxidising substances, the diazines are non-reactive towards oxidising agents, in particular towards atmospheric oxygen.

It has now been found that reduction products of 1,4-diazines reduced to at most the dihydro stage can be produced before or at the start and during the course of the photographic development by reduction of 1,4-diazine compounds with the help of reducing agents disposed in layers, e.g. incorporated into a layer, which are non-reactive to atmospheric oxygen. The process in accordance with the present invention for the photographic development of silver salts to metallic silver with the help of 1,4-diazine compounds reduced to at most the dihydro stage is thus characterised in that these diazine developer substances are produced only before the developing process and during the developing process from diazine compounds reduced to less than the dihydro stage, in acid medium with the help of a reducing agent disposed in a layer of the material under treatment.

The reducing agents to be used in accordance with the invention are most conveniently metals, preferably metals which in the electro chemical series of elements are located above silver and below aluminium.

The redox standard potential of the following electrochemical half cell reaction



should preferably, for the metals used, be at most +0.53 volt. In the above redox equation for a metal-metal ion pair, M is the metal, M^{n+} the corresponding metal ion, e^- is the symbol for the electron, and n is the number of the electrons entering the half cell reaction.

Consequently, the most suitable metals for the invention are copper and all those metals which in the electrochemical series of elements are situated above copper, i.e. the metals which precipitate copper from a solution of copper salt. Among these are, e.g., iron, cobalt, nickel, lead and tin.

Among these metals those are preferred which do not react rapidly at room temperature with oxygen or in neutral medium with water. The inactivity of various metals, especially towards oxygen, may be due to thermodynamic reasons or, may be due to an excessive activation energy required for oxidation or may be due to the fact that the metal is coated with an impermeable layer. Thus, e.g. aluminium metal is protected from further oxidation by a thin layer of oxide.

The reducing agents to be used in accordance with the invention are preferably distributed in layer form in the photographic material containing the silver salt to be developed.

The metals may be distributed in the form of small particles in a layer containing silver salt or, possibly, in an adjacent auxiliary layer. Auxiliary layers may be joined inseparably to, or be readily separable from, the silver salt emulsion layer. The particles may be dispersed directly in a colloid layer or they may be additionally surrounded by a cover of a polymer substance. Furthermore the metal particles may be contained in capsules that can be broken open by changes of pressure, temperature or pH. Furthermore, the metals may be applied in the form of small particles of a polymer substance which are coated with a cover of the metal. Also, the metal may be vapour-deposited as a layer on a support or be rolled out into film or be present in the form of sheets.

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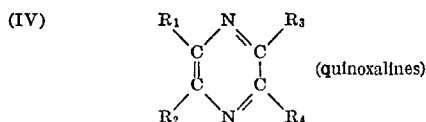
Another embodiment of the invention consists in that the reducing agent required for the reduction of the 1,4-diazine compounds is applied to an auxiliary layer and that this auxiliary layer, for development, is brought into contact with the layer containing the silver salt in the presence of an acid medium.

A further embodiment of the invention consists in that the metal required for the reduction of the 1,4-diazine compounds is contained in finely divided form in a paste or on a Bimat band which for development as applied in a thin layer to the material containing the silver salt.

It is also possible in accordance with the invention to use mixtures of metals and alloys of metals.

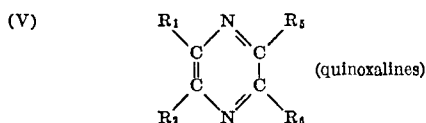
It is appropriate to use in the present process 1,4-diazines which contain, at least one ring of Formula I.

Thus, e.g., basic diazines of the formula

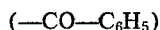


may be used wherein R_1 and R_2 together form a six-membered aromatic-carbocyclic ring and R_3 and R_4 represent hydrogen atoms, alkyl groups with preferably a maximum 3 carbon atoms (especially methyl groups), phenyl residues or heterocyclic residues. R_3 and R_4 may be different but are preferably the same.

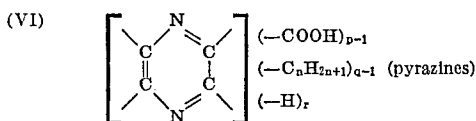
Furthermore basic diazines of the formula



may be used, wherein R_1 and R_2 together form a six-membered aromatic carbocyclic ring, R_3 represents a hydrogen atom or preferably an alkyl group, especially a methyl group, or a phenyl residue and R_4 an acetyl group ($-\text{CO}-\text{CH}_3$) or a benzoyl group

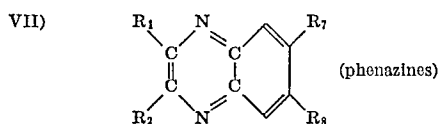


A further group of diazines corresponds to the formula:



wherein n , p and q are whole numbers, each of a value at most 3 and $r+6-p-q$. n is preferably 1 and $p+q$ preferably at most 4.

Finally, mention should be made of the basic diazines of the formula

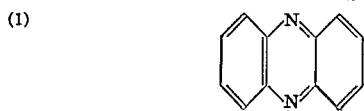


wherein R_1 and R_2 together form a six-membered aromatic, carbocyclic ring, R_7 and R_8 each represent a hydrogen atom or R_7 represents an NH_2 group and R_8 also an NH_2 group or a OH -group.

The carbocyclic six-membered rings formed by R_1 and R_2 together with two carbon atoms of the diazine ring of the Formulae IV, V and VI may contain further substituents such as methyl groups, methoxy groups or halogen atoms but are preferably free of substituents.

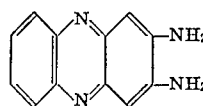
Examples of diazines which can be used in the process of the present invention are set out below:

PHENAZINES



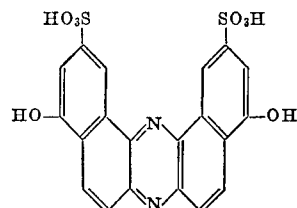
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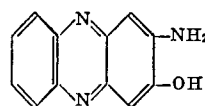
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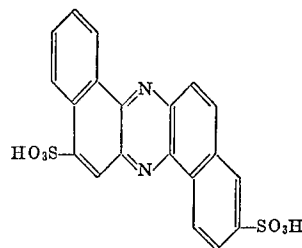
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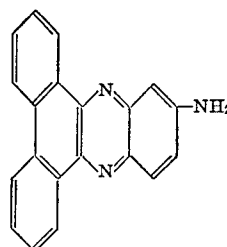
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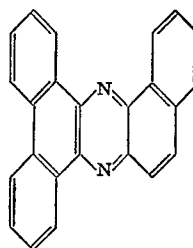
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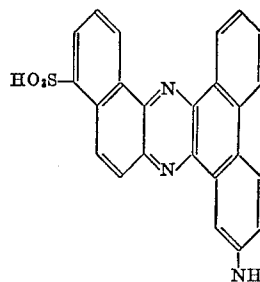
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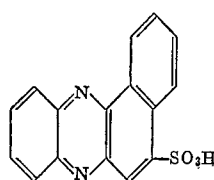
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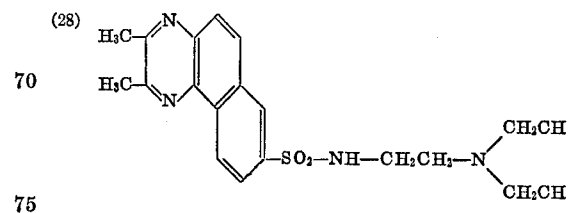
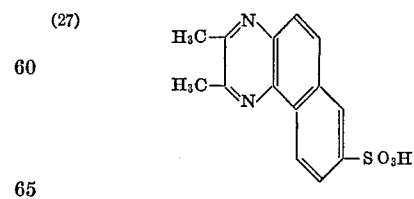
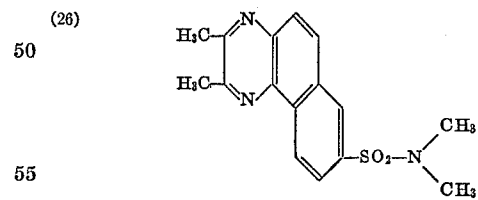
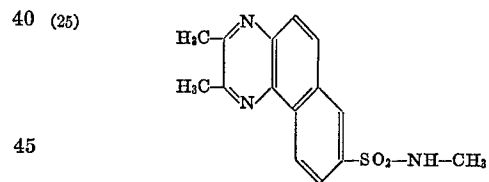
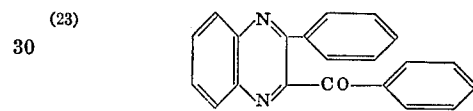
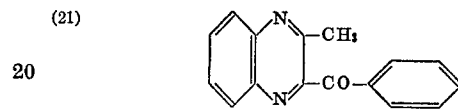
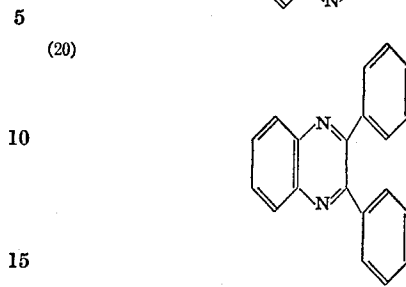
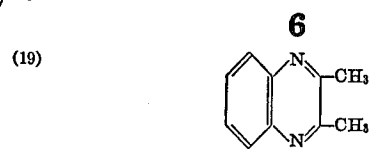
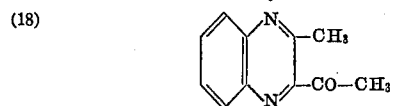
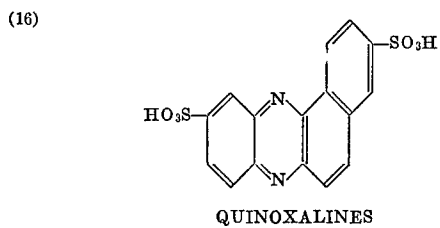
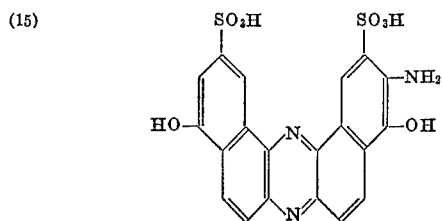
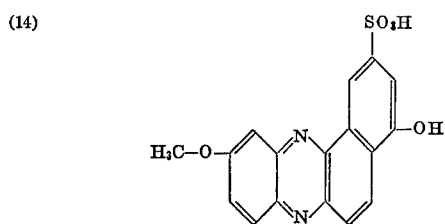
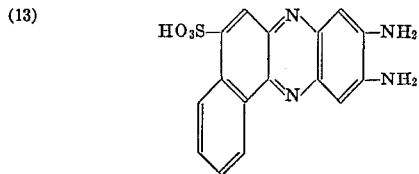
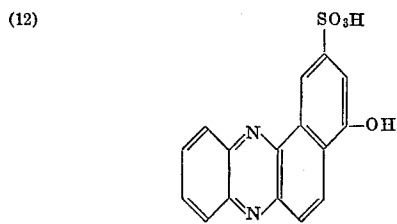
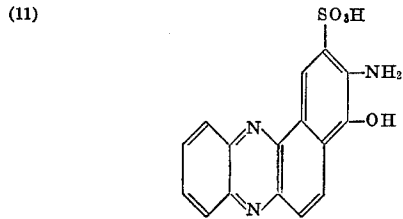
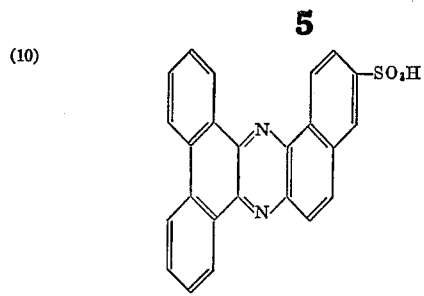
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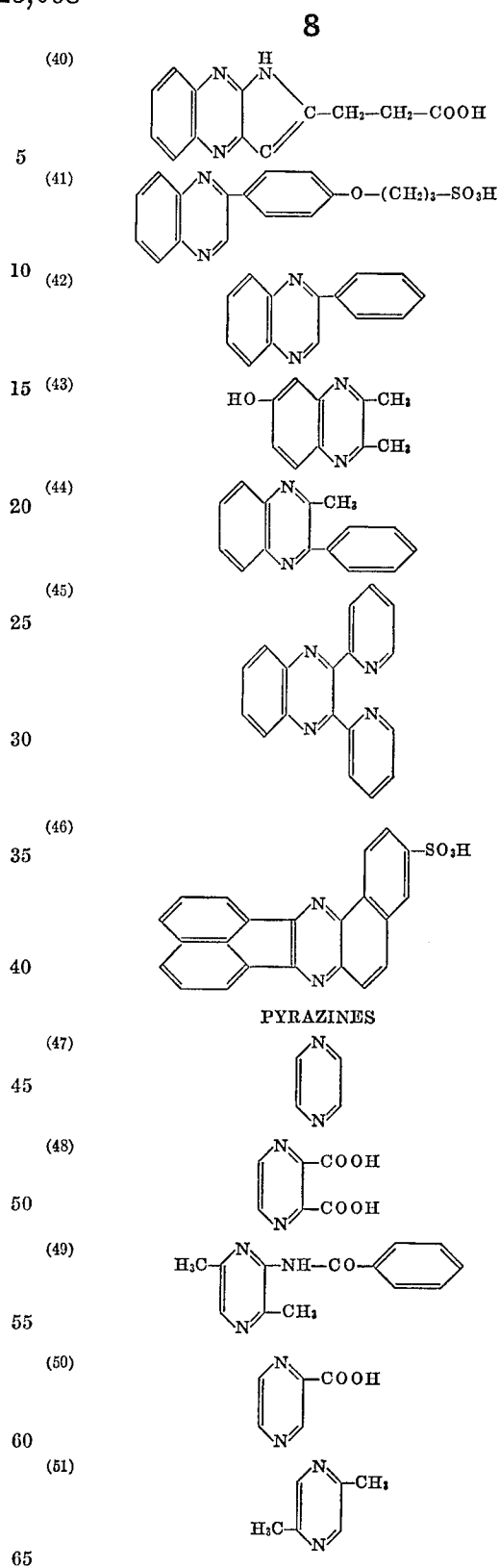
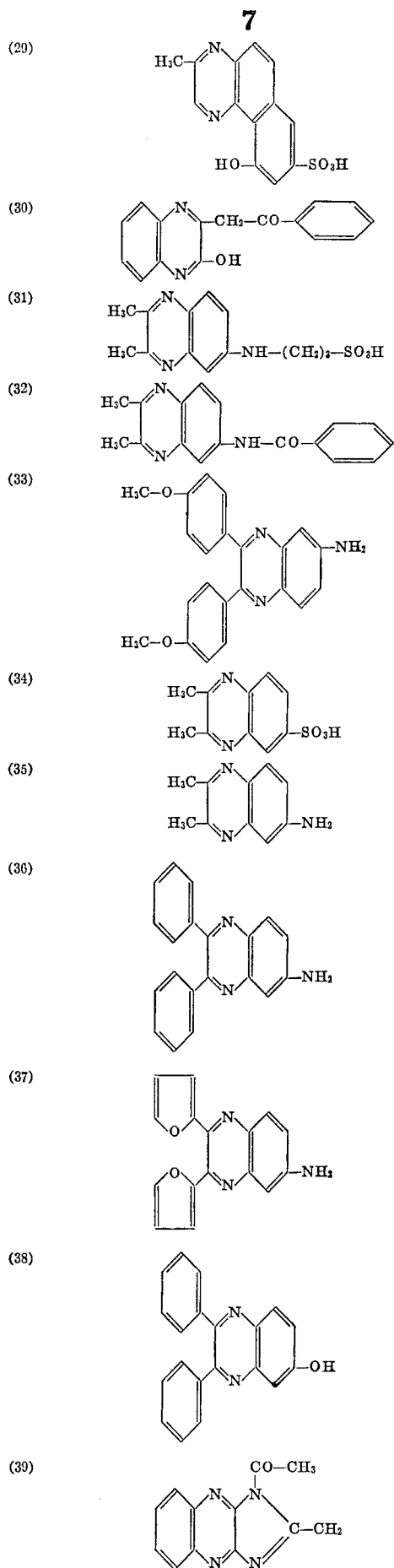
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Instead of the 1,4-diazines it is also possible to use the N-oxides derived from these, which in a first stage are reduced to the diazines and then react like the latter.

Particularly well suited for the present process are
 70 quinoxalines, pyrazines and phenazines which are unsubstituted or substituted by 1 or 2 low alkyl groups, one low alkyl group and a carboxyl group or acetyl group, a carboxyl group, an acetyl group or a d-arabotetrahydroxybutyl group, e.g. pyrazine, 2,3-dimethyl quinoxaline,
 75 2-methyl-3-acetylquinoxaline, 2-phenyl quinoxaline, quin-

oxaline, pyrazine-2-carboxylic acid, phenazine or 2-(*d*-arabotetrahydroxybutyl)-quinoxaline.

The process is preferably effected in aqueous medium, adjusted by a suitable acid or a buffer mixture to acid reaction, preferably to a pH value between 0 and 4. The rate of development and the gradation (compost of the developed image) may be altered within wide limits as function of the pH value. The following acids and buffer substances are exemplary:

Aliphatic, aromatic or heterocyclic mono-, di- and tri-carboxylic acids which may also contain substituents such as chlorine, bromine and iodine atoms, hydroxyl-, nitro-, amino- or acylamino groups; aliphatic or aromatic sulphonic acids, phosphoric acids, ammonium ions, and HSO_4^- , HF , HCl , HBr , HClO_4 , HNO_3 , H_2SO_4 , H_3PO_4 , H_2CO_3 , HSO_3^- , SO_2 , $\text{Al}(\text{H}_2\text{O})_6^{3+}$, HBF_4 , $\text{Na}_2\text{S}_2\text{O}_7$, $\text{Na}_2\text{S}_2\text{O}_5$.

As mentioned previously, the 1,4-diazine compounds may be used as aqueous solutions. The solution may contain a mixture of two or more diazines. The diazines may also be applied to act on the metal by impregnating an absorbent band with the solutions or by disposing the *m*, in suspension or dissolved in a high-boiling solvent, in the form of droplets. Furthermore the diazines may be incorporated in the light-sensitive layer or in an adjacent layer in capsules which can be broken open by changes of the pressure, temperature or the pH, or they may be contained in frangible containers between the layers of film packs for the diffusion transfer process.

Furthermore the diazines may be brought to act on the metal in the form of solutions which contain silver halide solvents such as bromide ions, thiocyanate ions or thiourea in suitable concentration. Anti-foggants such as benzotriazole or phenyl mercaptotetrazole may also be added. Hardening agents for gelatin, toning substances for the generation of a blue-black silver image and surface-active substances may also be added to the solution.

Of particular importance are those additions however, which raise the reactivity of the metal towards the diazine compounds.

If suitable agents, so-called ligands are added to the solution containing diazine, which form with the oxidation product of the metal used for the reduction of the diazine, namely the metal ion, complexes or difficultly soluble precipitates, the metal becomes a stronger reducing agent than it would be in the absence of the ligand. Such ligands may also be used for dissolving coating present on the metal surface, especially coatings of metal oxide or metal sulphide.

Thus for example the fluoride ion forms complexes with aluminium (III) ions, the copper (I) ion is bonded into a complex by ligands such as nitriles, olefins, chloride ions, bromide ions and thio ethers. A large number of ligands, together with the constants of stability of the complexes they form with various metal ions are contained in the book, "Stability Constants of Metal Ion Complexes, Special Publications No. 17, London: The Chemical Society, Burlington House, W.1, 1964."

The developer substances produced in accordance with the invention by reduction of 1,4 diazine compounds with the help of metal arranged in a layer or distributed in a layer are suitable for the development of any silver halide emulsions, e.g. those from silver chloride, silver bromide, silver chlorobromide or silver iodobromide, the emulsions in the customary layer formers, preferably gelatin, also containing the customary additives such as sensitizers and surface-active substances and being sensitive to the most varied rays of corpuscular or electromagnetic nature. Silver salts free of binders which have been vapour-deposited onto a support can also be developed in accordance with the invention.

The term "development" is to be understood here to means generally the liberation of silver from silver salts contained in layer materials, that is to say not only the selective reduction of imagewise exposed silver halide crystals, but also the reduction of silver salts in diffusely

exposed layers and the reduction of silver salts which can be developed without exposure, such as, e.g., rehalogenised silver or silver salts with fog nuclei, as are present for example in chemically aged emulsions. Likewise the secondary development in the reversion process, the physical development in the metal diazo process or the reduction of dissolved silver salts in the positive layer of the silver salt transfer process, where silver salts are reduced in contact with colloid metal or sulphide, can be carried out in accordance with the present process. It is also possible in accordance with the invention to use mono baths for the so-called stabilisation process. Furthermore the process is advantageous for surface development in direct positive methods which are based on the principle of a latent internal image; such methods have been described, e.g., in United States patent specifications Nos. 2,456,953 and 2,479,875 and in Dutch patent applications Nos. 6605890 and 6605891.

Of particular importance are those embodiments of the process in accordance with the invention wherein the developed silver image, the undeveloped silver salt image which is oppositely oriented to the developed silver image, or the corresponding distribution of unused developed substance in the silver salt image, or the used developer substance, which is distributed imagewise, are used for the promotion of further chemical reactions, whereby pictures are formed which are based on dye formation, dye decomposition, differences in the degree of polymerisation of the layer colloid, variable electrical conductivity, variable diffusibility (e.g. silver complex diffusion process) or sublimability, in particular differential dissolving or etching of metals and alloys reducing 1,4-diazine compounds. Of particular importance is the production of coloured pictures.

The reduction products of the 1,4-diazine compounds are suitable at the same time for reducing azo dyes, such as are used in the silver dye bleaching process is picture dyes. By choosing suitable reduction conditions it is possible in one layer, which besides silver halide also contains a reduceable azo dye, to reduce on the exposed areas preferably the silver halide, whilst on the unexposed areas the dye is reduced. In this manner, beside the silver image, an equidirectional dyestuff image is produced. Instead of the azo dyes other reduceable compounds, such as diazonium salts, nitro compounds or quinones may be imagewise reduced at the unexposed areas.

Another important aspect is the production of metal images which consist of metals other than silver.

In the course of the development of silver from silver salt, reduction products of 1,4-diazine, reduced to at most the dihydro stage, which serve as developer substances, are reoxidised to the diazine. Thus in the light-sensitive layer a distribution of 1,4-diazine compound is formed which is equidirectional to the developed silver image. The diazine compound is reduced again by the metal distributed in layer form used as reducing agent, and metal is thereby consumed. The result of this is that, on development in accordance with the process of the invention a metal image is formed which does not consist of silver, and is oppositely oriented to the developed silver image.

In the process in accordance with the invention, the 1,4-diazine compounds act as redox catalysts, in that their reduction products, reduced at most to the dihydro stage, transfer electrons from the metal which is in layer form and used as reducing agent, onto the silver salt. Very small concentrations of the 1,4-diazine compound are already sufficient, therefore, in order to liberate silver from the silver salt in accordance with the process of the invention and, at the same time, to dissolve the metal which is arranged in layer form and used as a reducing agent, imagewise.

Moreover, many new possibilities result from a combination of the present process with known development processes which take place in alkaline medium. Thus, for example, in a chromogenic reversal process the primary development can be carried out in accordance with the

invention in acid medium with the reduced 1,4-diazine compounds and the chromogenic development can take place in accordance with known methods. Other novel effects can be achieved by the combination of layer colloids with various swelling and diffusion characteristics as a function of the pH value or by the use of filter layers soluble only in alkaline medium, which, after the first acid development, preserve their optical effectiveness and are eliminated only in a later stage of the process.

The following examples will serve to illustrate the invention:

EXAMPLE 1

A strip of a light-sensitive material, consisting of a gelatin layer containing finely divided copper metal and applied to a polyester support, and a silver bromide emulsion layer arranged above this layer, is exposed behind a step wedge and is then dipped during 5 minutes into a bath of the following composition:

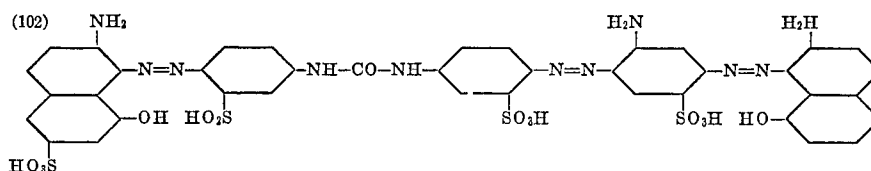
Pyrazine—16 g.
Sulphamic acid—120 g.
Acetonitrile—160 ml.
Polyethylene glycol—24 g.
Water—to 1000 ml.

The strip is then dipped during 30 seconds into a ten percent aqueous solution of sodium acetate trihydrate, washed and then treated during 2 minutes with an acid thiosulphate fixing bath so as to remove undeveloped silver bromide. The strip shows a silver image of the step wedge used for exposure, which is negative in respect of the original. The strip is then washed and subsequently dipped during two minutes into a bath of the following composition so as to remove any remaining metallic copper:

Ammonium-ferri-sulphate dodecahydrate—50 g.
Sulphuric acid 2 N—50 ml.
Water—to make 1000 ml.

EXAMPLE 2

A strip of the light-sensitive material described in



Example 1 is exposed behind a grey wedge and is then dipped during 6 minutes into a solution of the following composition:

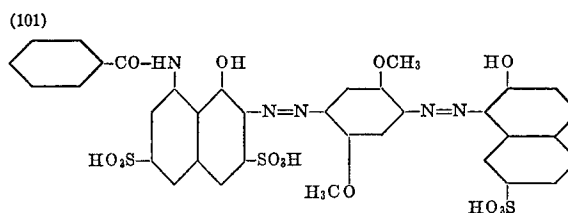
2,3 dimethyl quinoxaline dissolved in 14 ml. of dimethyl formamide—10 g.
Nitric acid 2 N—120 ml.
2,2' bipyridyl—7 g.
Polyethylene glycol—20 g.
Water—to 1000 ml.

Subsequently the strip is dipped during 30 seconds into a ten percent aqueous solution of sodium acetate-tri-hydrate and is then fixed in a known manner by an acid thiosulphate solution.

The strip presents a silver image of the grey wedge used for exposure which is negative in respect to the original.

EXAMPLE 3

A strip of a light-sensitive material consisting of a gelatin layer containing finely divided metallic copper and applied to a polyester base and a silver bromide emulsion layer containing the blue-green dye of the formula:



arranged above it, is exposed behind a step wedge and is then treated during 3 minutes with a solution of the following composition:

2 methyl-3-acetyl quinoxaline dissolved in 20 ml. dimethyl formamide—3 g.
Perchloric acid 70%—35 ml.
Vinyl acetic acid—200 ml.
Water—to 1000 ml.

A silver image negative in respect to the original, and at the same time a blue-green dye image negative to the original, are formed.

The strip, after short washing, is treated with a bleach liquor for copper and silver of the following composition:

Potassium hexacyano ferrate—75 g.
Potassium bromide—15 g.
Primary sodium phosphate monohydrate—10 g.
Sodium acetate-tri-hydrate—5 g.
Glacial acetic acid—10 ml.
Water—to 1000 ml.

This is followed by washing and fixing by an acid thio-sulphate solution.

The strip presents a blue-green image of the step wedge used for exposure which is negative in respect to the original.

EXAMPLE 4

A strip of a light-sensitive material, consisting of a gelatin layer containing finely divided metallic copper and applied to a transparent base, and a silver bromide emulsion layer containing a purple-red dyestuff of the formula

arranged above it, is exposed behind a step wedge and is then treated for the development of the exposed silver bromide during 150 seconds with a solution of the following composition:

2-methyl-3-acetyl quinoxaline, dissolved in 20 ml. dimethyl formamide—3 g.
Perchloric acid 70%—35 ml.
Allyl alcohol—145 g.
Polyethylene glycol—20 g.
Water—to 1000 ml.

A silver image which is negative in respect to the original is formed, and at the same time a purple-red dye image which is negative in respect to the original.

After washing for half an hour the image is fixed by a thiosulphate solution in known manner. The strip presents a dye image which is negative in respect to the original and at the same time a silver image of the step wedge used for exposure which is negative in respect to the original.

EXAMPLE 5

A strip of the light-sensitive material described in Example 4 is exposed behind a grey wedge and is then

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treated for the development of the exposed silver bromide and for the simultaneous imagewise bleaching of the dye during 11 minutes with a bath of the following composition:

2-(d-arabotetrahydroxybutyl)-quinoxaline—1.5 g.
Sulphamic acid—60 g.
Sodium chloride—58.5 g.
Polyethylene glycol—20 g.
Water—to 1000 ml.

The further processing is as in Example 4.

The purple-red colour image is obtained and at the same time a silver image of the step wedge used for exposure. Both images are negative in respect to the original.

EXAMPLE 6

The procedure is as in Example 5, except that for the development of the imagewise exposed silver halide and for the simultaneous bleaching of the dye a treatment of 2.5 minutes in a bath of the following composition is used:

2-methyl-3-acetyl quinoxaline, dissolved in 20 ml. dimethyl formamide—3 g.
Perchloric acid 70%—45 ml.
Sodium salt of the Formula 103
 $(\text{CH}_3\text{—CH}_2\text{—S—CH}_2\text{—CH}_2\text{—CH}_2\text{—SO}_3\text{—Na})\text{—20 g.}$
Polyethylene glycol—20 g.
Water—to 1000 ml.

The strip presents a purple-red colour image which is negative in respect to the original and at the same time a silver image, negative in respect to the original, of the step wedge used for bleaching.

EXAMPLE 7

A strip of a light-sensitive material which consists of a gelatin layer containing finely divided metallic nickel and applied to a plastic base, and a silver halide emulsion layer containing the purple-red dye mentioned in Example 4 and arranged above this layer, is exposed behind a step wedge and is then dipped during 20 minutes for the purpose of the imagewise reduction of the silver halide to silver, and the simultaneous bleaching of the dyestuff, into a bath of the following composition:

Pyrazine—10 g.
Sulphamic acid—60 g.
Polyethylene glycol—20 g.
Water—to 1000 ml.

Then the strip is washed and fixed by a thiosulphate solution in known manner.

The strip presents a purple-red colour image which is negative in respect to the original and at the same time a silver image of the step wedge used for exposure which is negative to the original.

EXAMPLE 8

A strip of a light-sensitive material, which consists of a gelatin layer containing finely divided metallic cobalt and applied to a transparent base, and of a silver bromide emulsion layer containing the purple-red dyestuff mentioned in Example 4 and arranged above this layer, is exposed behind a grey wedge and is then dipped during 5 minutes into a solution of the following composition:

Pyrazine—10 g.
Sulphamic acid—60 g.
Water—to 1000 ml.

The strip is then washed and is subsequently fixed by an acid thiosulphate solution in known manner.

The strip presents a silver image negative in respect to the original and at the same time a purple-red colour image which is negative in respect to the original.

For the removal of the silver image the strip, after a renewed washing, is dipped for one minute into the silver

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bleach bath described in Example 3, then it is washed and then it is treated by an acid thiosulphate fixing bath.

The strip presents a purple-red image of the grey wedge used for exposure which is negative in respect to the original.

EXAMPLE 9

A strip of a light-sensitive material which consists of metallic cobalt vapour-deposited in the form of a thin layer onto a polyester foil, and a silver bromide emulsion layer arranged on top of it, is exposed behind a step wedge and is then dipped for the development of the silver bromide exposed in accordance with the image, into a solution of the following composition.

Pyrazine—10 g.
Sulphamic acid—60 g.
Polyethylene glycol—20 g.
Water—to 1000 ml.

After one minute the strip is washed. Subsequently it is fixed by a thiosulphate solution and then washed again. The strip presents a silver image of the step wedge used for the exposure, which is negative in respect to the original.

Metallic cobalt which has not been used in the course of the development is then removed by a solution of the following composition:

Ferriperchlorate-nonahydrate—55 g.
Perchloric acid 70%—15 ml.
Water—to 1000 ml.

EXAMPLE 10

A strip of a light-sensitive material consisting of a gelatin layer containing finely divided metallic iron and applied to a plastic foil, and of a silver bromide emulsion layer containing the purple-red dyestuff mentioned in Example 4, and arranged on top of this layer, is exposed behind a step wedge. The further processing is as in Example 8, except that the time of action of the bath serving for the imagewise reduction of the silver halide and the simultaneous imagewise decomposition of the dyestuff is limited to one minute.

The strip presents a purple-red colour image which is negative in respect to the original and at the same time a silver image of the step wedge used for exposure which is negative in respect to the original.

EXAMPLE 11

A strip of a light-sensitive material consisting of metallic lead, vapour-deposited in form of a thin layer onto a carrier film and a silver bromide emulsion layer arranged on top of it, is exposed behind a grey wedge and is then dipped for one minute into the bath described in Example 9 serving for the reduction of the silver bromide in accordance with the image.

The strip is then washed and fixed in known manner by thiosulphate solution.

The strip presents a silver image of the grey wedge used for exposure which is negative in respect to the original.

EXAMPLE 12

A strip of a light-sensitive material consisting of a layer of metallic tin, vapour-deposited on a polyester carrier and a silver bromide emulsion layer containing the blue-green dyestuff mentioned in Example 3 and arranged on top of it, is exposed behind a step wedge and is then dipped for 15 seconds into a bath of the following composition:

Pyrazine—10 g.
Sulphamic acid—60 g.
Water—to 1000 ml.

The strip is treated for one minute with a solution of the following composition for the purpose of removing

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metallic tin still present in the material, developed silver and undeveloped silver:

Sodium-ferri-ethylenediamine tetra-acetate—50 g.
Sodium sulphite—10 g.
Ammonium fluoride—200 g.
Sulphuric acid 2 N—to pH=5.
Ammonium thiosulphate—120 g.
Sodium acetate trihydrate—25 g.
Acetic acid—13 ml.
Water—to 1000 ml.

The strip presents a blue-green colour image which is negative in respect to the original step wedge used for exposure.

EXAMPLE 13

A strip of a light-sensitive material consisting of a layer of metallic tin, vapour-deposited onto a plastic foil and a silver chloride emulsion layer arranged on top of it, is exposed behind a step wedge.

A gelatin layer containing colloidal silver and applied to a transparent base, which serves as a picture receiving layer, is moistened by dipping into a solution of the following composition:

Pyrazine—10 g.
Sulphamic acid—20 g.
Potassium chloride—7 g.
Thiourea—0.4 g.
Water—to 1000 ml.

and is then brought into contact, for 2 minutes under light pressure with the exposed silver chloride emulsion. Then the picture receiving layer and the emulsion layer are separated again from one another.

The picture receiving layer presents a positive silver image of the step wedge used for the exposing of the light-sensitive material. The exposed strip on the other hand presents a silver image of the step wedge which is negative in respect to the original.

EXAMPLE 14

A strip of a light-sensitive material consisting of a silver bromide emulsion containing the blue-green dye-stuff mentioned in Example 3 and applied onto a cellulose triacetate base, is exposed behind a step wedge and is then moistened by brief dipping into a solution of the following composition:

Pyrazine—10 g.
Sulphamic acid—20 g.
Water—to 1000 ml.

The emulsion layer of the strip is brought into contact during 5 seconds with a foil of metallic lead and is then separated again from the lead foil.

The strip is fixed by a thiosulphate solution and subsequently washed.

The strip presents a blue-green colour image as well as a silver image of the step wedge used for exposure. The colour image and the silver image are negative in respect to the original.

EXAMPLE 15

A strip of a commercial black and white negative film is exposed behind a step wedge and is then moistened with a solution of the following composition:

Pyrazine—10 g.
Sulphamic acid—20 g.
Water—to 1000 ml.

Subsequently the emulsion layer of the strip is brought into contact for 5 seconds with a layer of metallic tin, vapour-deposited onto a polyester base and then separated again from the tin layer.

Subsequently the strip is treated with a thiosulphate bath and then washed.

The strip presents a silver image which is negative in respect to the original. The tin layer used for the develop-

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ment is etched during the development in accordance with the image, so that a tin image which is positive in respect of the original is obtained.

EXAMPLE 16

5 A strip of a light-sensitive material consisting of a silver bromide emulsion layer containing pyrazine and the blue-green dyestuff mentioned in Example 3 and applied to a carrier film, is exposed behind a step wedge.

10 Then the emulsion layer of the strip is brought into contact for 30 seconds with a paste of the following composition applied to a plastic support:

Carboxymethyl cellulose—10 g.
Water—100 g.
15 Cobalt powder—15 g.
Sulphuric acid 2 N—to pH=0.7

Then the strip is dipped during half a minute into a thiosulphate fixing bath and then it is washed.

20 The strip presents a blue-green colour image and a silver image of the step wedge used for exposure. Both images are negative in respect to the original.

EXAMPLE 17

25 A strip of a silver bromide emulsion layer applied to a transparent cellulose triacetate support is exposed behind a step wedge and is then dipped for 30 seconds into a solution of the following composition:

Pyradine-N-oxide—1 g.
30 Sulphamic acid—2 g.
Hydrochloric acid (37%)—1 ml.
Polyethylene glycol-tert.-dodecylthioether—1 drop.
Water—to 100 ml.

35 Subsequently the moist emulsion layer is brought into contact with a tin foil for the purpose of reducing the exposed silver halide to metallic silver.

After 10 seconds the strip is separated from the tin foil, washed with water and subsequently fixed in known manner by an ammonium thiosulphate solution.

40 The strip presents a silver image which is negative in respect to the original.

EXAMPLE 18

45 The procedure is as in Example 17, except that the strip after exposure is dipped during 30 seconds into a solution of the following composition:

Pyrazine-di-N-oxide—1.1 g.
Sulphamic acid—2 g.
50 Hydrochloric acid 37%—1 ml.
Octylphenolpolyethylene glycol (with 9–10 mol ethylene oxide)—1 drop.
Water—to 100 ml.

55 As in Example 17 a negative silver image of the step wedge used for exposure is obtained.

EXAMPLE 19

60 The procedure is as in Example 17, except that the strip after exposure is dipped for 30 seconds into a solution of the following composition:

2,5 dimethyl pyrazine—1 g.
Sulphamic acid—2 g.
Hydrochloric acid 37%—1 ml.
65 Polyethylene glycol tert. dodecyl thioether—1 drop
Water—to 100 ml.

EXAMPLE 20

70 A strip of the light-sensitive material described in Example 17 is exposed behind a step wedge and is then dipped for 30 seconds into a solution of the following composition:

Phenazine—0.5 g.
Dissolved in tetrahydrofurane—50 ml.
75 Citric acid monohydrate—10.5 g.

Sodium hydroxide—1 g.
Water—50 ml.

The wet emulsion layer of the strip is then brought into contact with a tin foil for the development of the silver image. After 4 minutes the strip is separated from the tin foil, washed with water and then fixed by an acid thiosulphate solution. The strip presents a silver image which is negative in respect to the original.

EXAMPLE 21

A strip of a commercial photographic enlarging paper is exposed behind a step wedge and is then dipped for 30 seconds into a solution of the following composition:

Pyrazine-2-carboxylic acid—0.25 g.
Dissolved in ethanol—100 ml.
Sulphuric acid—0.1 ml.
Octylphenol polyethyleneglycol (with 9-10 mol ethylene oxide)—1 drop.

Subsequently the moist emulsion layer of the strip is brought into contact with a bright iron sheet for the purpose of the reduction of exposed silver halide to metallic silver. After 5 minutes the strip is separated from the iron sheet, washed with water and subsequently fixed in known manner by a thiosulphate solution.

The strip presents a silver image which is negative in respect to the original.

What is claimed is:

1. In the process for the photographic development of silver salts to metallic silver by contacting exposed silver salts in acid medium with a 1,4-diazine compound reduced at most to the dihydro stage and subject to oxidation, the improvement which comprises: forming said 1,4-diazine compound reduced at most to the dihydro stage in the presence of said exposed silver salts by contacting a 1,4-diazine compound reduced to less than the dihydro stage with a layer of a metal above silver and

below aluminum in the electrochemical series of elements.

2. A process in accordance with claim 1, wherein said metal is selected from the group consisting of iron, cobalt, nickel, lead, tin or copper.

3. A process in accordance with claim 1, wherein the 1,4-diazine compound reduced to less than the dihydro stage is selected from the group consisting of pyrazines, quinoxalines and phenazines.

4. A process in accordance with claim 1, wherein the metal is present in a layer containing the silver salt.

5. A process in accordance with claim 1, wherein the metal is present in a layer adjacent to layer containing the silver salt.

6. A process in accordance with claim 5, wherein the layer containing the metal is brought into contact with a layer containing silver salt only during the development.

7. A process in accordance with claim 1, wherein the 1,4-diazine compounds reduced to less than the dihydro stage are produced with the aid of said metal arranged in layer form in the presence of ligands which form complexes or difficultly soluble precipitates with said metal.

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